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(54) Title: FLUOROCARBON REFRIGERANT COMPOSITIONS

(57) Abstract: The invention provides fluorocarbon refrigerant compositions that offer alternatives, and are considered environmentally safe substitutes, for CFC's and HCFC's. The compositions of the invention are useful as refrigerants, including for use in chillers, aerosol propellants, metered dose inhalers, heat transfer media, gaseous dielectrics, fire extinguishing agents, foam blowing agents, solvents and sterilants. The compositions of the invention are soluble in lubricating oils and are, therefore, particularly useful as R-22 retrofit fluids.

FLUOROCARBON REFRIGERANT COMPOSITIONS

Field of the Invention

The invention relates generally to compositions for use as refrigerants, 5 including for use in chillers, aerosol propellants, metered dose inhalers, heat transfer media, gaseous dielectrics, fire extinguishing agents, foam blowing agents, solvents and sterilants. The compositions are particularly useful as R-22 retrofit fluids in that they are soluble in lubricating oil.

Background of the Invention

10 Fluorocarbon based fluids have found widespread use in industry in a number of applications, including as refrigerants, aerosol propellants, blowing agents, heat transfer media, gaseous dielectrics, fire extinguishing agents, foam blowing agents, solvents and sterilants. Because of the suspected environmental problems associated with the use of some of these fluids, it is desirable to use fluids of lesser ozone 15 depletion potential such as hydrofluorocarbons, ("HFC's") and/or hydrochlorofluorocarbons ("HCFC's"). The art continually is seeking new fluorocarbon based mixtures that offer alternatives, and are considered environmentally safe substitutes, for CFC's and HCFC's. Of particular interest are mixtures containing a fluorocarbon and hydrochlorocarbon both of low ozone 20 depletion potentials; it is these mixtures that are the subject of this invention.

The use of fluorocarbon based fluids for refrigeration, air conditioning and heat pump applications is known. See, for example, U.S. Patent Nos. 4,978,467; 5,277,934; 5,211,867; 5,403,504; 4,943,388; 5,370,811; 4,303,536; 4,482,465; 25 5,433,879; 5,188,749, herein incorporated by reference in their entirety.

The widespread commercial use of chlorine-free hydrofluorocarbon refrigerants has been hindered, however, by the lack of commercially adequate lubricants. Mineral oil or alkyl benzenes, which have been used traditionally with R-22, are immiscible with R-407C and must therefore be replaced with expensive

polyol ester lubricants. In retrofitting refrigerant systems with hydrofluorocarbon refrigerants it is necessary to drain as much of the oil as possible before adding the replacement lubricant. Often this entails removing the compressor from the system to drain lubricant. A chlorine-free R-22 retrofits that is soluble in lubricating oil would 5 advance the art.

The use of fluorocarbon based fluids in sterilant mixtures is known. See, for example, U.S. Patent Nos. 5,976,554; 5,376,333; 4,976,922; 5,039,484; 5,039,485; 5,342,579; and 5,254,309, herein incorporated by reference in their entirety.

10 The use of fluorocarbon based fluids as blowing agents is known. See, for example, U.S. Patent Nos. 5,946,866; 5,688,833; 5,759,438; and 5,925,612, herein incorporated by reference in their entirety.

The use of fluorocarbon based fluids as solvents is known. See, for example, U.S. Patent Nos. 5,219,490; and 4,842,764, herein incorporated by reference in their entirety.

15 The use of fluorocarbon based fluids as fire extinguishing agents is known. See, for example, U.S. Patent Nos. 5,918,680; 4954,271; 5,135,054 and 5,135,054; herein incorporated by reference in their entirety.

20 The use of fluorocarbon based fluids as aerosol propellants and in metered dose inhalers is known. See, for example, U.S. Patent Nos. 6,013,245; 5,891,419; and 5,858,331, herein incorporated by reference in their entirety.

Summary of the Invention

25 The invention provides fluorocarbon refrigerant compositions that offer alternatives, and are considered environmentally safe substitutes, for CFC's and HCFC's.

The compositions of the invention are soluble in lubricating oils and are, therefore, particularly useful as R-22 retrofit fluids.

The compositions of the invention comprise a refrigerant and a solubilizing agent. Preferably the refrigerant is a hydrofluorocarbon refrigerant. Optionally, the compositions of the invention further comprise a lubricating oil selected from the group consisting of mineral or hydrocarbon oil, alkyl benzene oil, white or paraffinic oil and mixtures thereof.

5 In one embodiment of the invention, there is provided a composition comprising a refrigerant selected from the group consisting of the compounds listed in Table 1 and mixtures thereof and at least one solubilizing agent selected from the group consisting of the compounds listed in Table 2 and mixtures thereof.

10 In another embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from the compounds listed in Table 1 and mixtures thereof; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds

15 listed in Table II and mixtures thereof.

20 In yet another embodiment of the invention, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from Table III; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds listed in Table II and mixtures thereof.

25 In still another preferred embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from Table IV; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the compounds listed in Table II and mixtures thereof.

30 In a particularly preferred embodiment, there is provided a composition comprising (i) from about 80 to about 99.9 weight percent, preferably from about 90 to about 99.9 weight percent, of a refrigerant selected from the group consisting of

R-407C, R-410A, R-404A and R-507A; and (ii) from about 20 to about 0.1 weight percent, preferably from about 10 to about 0.1 weight percent, of a solubilizing agent selected from the group consisting of butane, isobutane, pentane, dimethyl ether, and mixtures thereof.

5 When a lubricating oil is present, it is present in an amount of from about 1 to about 60 weight percent, preferably from about 10 to about 50 weight percent, based on the total composition.

10 In a process embodiment, there is provided a method for producing refrigeration which comprises condensing a composition of the invention and thereafter evaporating the composition in the vicinity of a body to be cooled.

In another process embodiment, there is provided a method for producing heating which comprises condensing a composition of the invention in the vicinity of a body to be heated and thereafter evaporating the composition.

15 In another embodiment, the compositions of the invention may be used in centrifugal chillers. By "centrifugal chillers" is meant refrigeration equipment that uses centrifugal compression to compress the refrigerant. The invention provides a method for producing refrigeration using a centrifugal compressor comprising compressing a refrigerant comprising the compositions of the invention and thereafter evaporating the refrigerant in the vicinity of a body to be cooled

20 In still another embodiment, the compositions of the invention may be used in a method for producing foam comprising blending a heat plasticized resin with a volatile blowing agent comprising the compositions of the invention and introducing the resin/volatile blowing agent blend into a zone of lower pressure to cause foaming.

25 In another process embodiment, the compositions of the invention are used in a method for producing polyurethane and polyisocyanurate foams. Any of the methods well known in the art such as those described in "Polyurethanes Chemistry and Technology," Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, 30 New York, NY. In general, the method comprises preparing polyurethane or polyisocyanurate foams by combining an isocyanate, a polyol or mixture of polyols, a

blowing agent or mixture of blowing agents, and other materials such as catalysts, surfactants, and optionally, flame retardants, colorants, or other additives. The blowing agent or agents employed shall be a volatile mixture of the compositions of the present invention.

5

It is convenient in many applications to provide the components for polyurethane or polyisocyanurate foams in preblended formulations. Most typically, the foam formulation is preblended into two components. The isocyanate and optionally certain surfactants and blowing agents comprise the first component, 10 commonly referred to as the "A" component. The polyol or polyol mixture, surfactant, catalysts, blowing agents, flame retardant, and other isocyanate reactive components comprise the second component, commonly referred to as the "B" component. Accordingly, polyurethane and polyisocyanurate foams are readily prepared by bringing together the A and B side components either by hand mix for 15 small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like. Optionally, other ingredients such as fire retardants, colorants, auxiliary blowing agents, water, and even other polyols can be added as a third stream to the mix head or reaction site. Most conveniently, however, they are all incorporated into one B 20 component as described above.

The compositions of the invention may also be used as heat transfer fluids. For example, in certain refrigeration systems, it is desirable to operate the system at a specific temperature. However, maintaining the desired temperature may require 25 either the addition or removal of heat. Thus, a secondary heating loop containing an appropriate heat transfer fluid may be added. The heat transfer fluid absorbs heat in one part of the cycle and transfers the heat to another part of the cycle without changing state, when the heat transferred is sensible, or by changing state, when the heat transferred is latent.

30

In another embodiment, the mixtures and compositions of this invention may be used as propellants in sprayable compositions, either alone or in combination with known propellants. The sprayable composition comprises, consists essentially of, and

consists of a material to be sprayed and a propellant comprising, consisting essentially of, and consisting of a mixture or composition of the invention. Inert ingredients, solvents, and other materials may also be present in the sprayable mixture.

Preferably, the sprayable composition is an aerosol. Suitable materials to be sprayed 5 include, without limitation, cosmetic materials such as deodorants, perfumes, hair sprays, cleansers, and polishing agents as well as medicinal materials such as anti-asthma and anti-halitosis medications.

The compositions of the invention may also be used in a method of dissolving 10 contaminants or removing contaminants from the surface of a substrate, which method comprises the step of contacting the substrate with the compositions of the present invention.

In another embodiment, the compounds and mixtures of the present invention 15 may also be used as fire extinguishing agents.

Detailed Description

The refrigerant may comprise any one of the compounds listed in Table I or mixtures of two or more thereof. Hydrofluorocarbon refrigerants are preferred. The 20 term hydrofluorocarbon refers to compounds composed solely of carbon, hydrogen and fluorine atoms. Of the hydrofluorocarbon refrigerants listed in Table I, R-32, R-143a, R-125, R-134a and mixtures thereof are preferred.

Refrigerant mixtures are preferred. Representative refrigerant mixtures are listed in Table III. Hydrofluorocarbon refrigerant mixtures are preferred. Of the 25 hydrofluorocarbon refrigerant mixtures listed in Table III, R-404A, R-407C, R-410A and R-507A are preferred. Hydrofluorocarbon refrigerant mixtures selected from Table IV are also preferred.

As used herein, the term solubilizing agent refers to a compound that increases the solubility of a hydrofluorocarbon refrigerant and a lubricating oil in one another. 30 It will be understood that the solubilizing agent may comprise any one of the compounds listed in Table II or mixtures of two or more thereof. Butane, isobutane

and dimethyl ether are preferred. The amount of solubilizing agent is an amount effective to dissolve a sufficient amount of refrigerant in the lubricating oil such that the diluted oil can be transported back to the refrigeration compressor. Typically, the solubilizing agent is present in an amount of from about 0.1 to about 20 weight percent, preferably from about 0.1 to about 10 weight percent, based on the total composition.

As used herein, the term lubricating oil refers to mineral or hydrocarbon oil; alkyl benzene oil; white or paraffinic oil; and mixtures thereof. Suitable lubricating oils are commercially available from various sources (e.g., Capella brand names from 10 Texaco and Suniso brand names from Sun Oil). The chemical compositions and uses of these oils are discussed in detail in the book "Fluorocarbon Refrigerants Handbook" by Ralph C. Downing, Prentice Hall, 1998, pp. 206-270. The amount of lubricating oil is an amount effective to provide acceptable lubrication to the compressor parts for its longevity. An effective amount of lubricating oil is the 15 amount recommended by the equipment manufacturer. Typically, the lubricating oil is present in an amount of from about 1 to about 60 weight percent, preferably from about 10 to about 50 based on the total composition.

Table I: Refrigerants

Refrigerant Number	Chemical Name	Chemical Formula
<i>Methane Series</i>		
11	Trichlorofluoromethane	CCl ₃ F
12	Dichlorodifluoromethane	CCl ₂ F ₂
13	Chlorotrifluoromethane	CClF ₃
14	Tetrafluoromethane (carbon tetrafluoride)	CF ₄
21	Dichlorofluoromethane	CHCl ₂ F
22	Chlorodifluoromethane	CHClF ₂
23	Trifluoromethane	CHF ₃
30	Dichloromethane (methylene chloride)	CH ₂ Cl ₂
31	Chlorofluoromethane	CH ₂ ClF
32	Difluoromethane (methylene fluoride)	CH ₂ F ₂
40	Chloromethane (methylene fluoride)	CH ₂ F ₂
41	Fluoromethane (methyl fluoride)	CH ₃ F
<i>Ethane Series</i>		
113	1,1,2-trichloro-1,2,2-trifluoroethane	CCl ₂ FCClF ₂
114	1,2-dichloro-1,1,2,2-tetrafluoromethane	CClF ₂ CClF ₂
115	Chloropentafluoroethane	CClF ₂ CF ₃
116	Hexafluoroethane	CF ₃ CF ₃
123	2,2-dichloro-1,1,1-trifluoroethane	CHCl ₂ CF ₃
124	1-chloro-1,1,1,2-tetrafluoroethane	CHClFCF ₃
125	Pentafluoroethane	CHF ₂ CF ₃
134a	1,1,1,2-tetrafluoroethane	CH ₂ FCF ₃
141b	1,1-dichloro-1-fluoroethane	CH ₃ CCl ₂ F
142b	1-chloro-1,1-difluoroethane	CH ₃ CClF ₂
143a	1,1,1-trifluoroethane	CH ₃ CF ₃
152a	1,1-difluoroethane	CH ₃ CHF ₂
<i>Propane Series</i>		
218	Octafluoropropane	CF ₃ CF ₂ CF ₃
227ea	1,1,1,2,3,3,3-heptafluoropropane	CF ₃ CHFCF ₃
236fa	1,1,1,3,3,3-hexafluoropropane	CF ₃ CH ₂ CF ₃
245fa	1,1,1-3,3-pentafluoropropane	CF ₃ CH ₂ CHF ₂
<i>Butane Series</i>		
365	1,1,1,3,3-pentafluorobutane	CF ₃ CH ₂ CF ₂ CH ₃
<i>Cyclic Organic Compounds</i>		
C318	Octafluorocyclobutane	-(CF ₂) ₄ -

Table II: Solubilizing Agents

Refrigerant Number	Chemical Name	Chemical Formula
<i>Miscellaneous Organic Compounds</i>		
<i>Hydrocarbons</i>		
30	Dichloromethane (methylene chloride)	CH ₂ Cl ₂
40	Chloromethane (methyl chloride)	CH ₃ Cl
50	Methane	CH ₄
170	Ethane	CH ₃ CH ₃
290	Propane	CH ₃ CH ₂ CH ₃
600	Butane	CH ₃ CH ₂ CH ₂ CH ₃
600a	Isobutane	CH(CH ₃) ₂ CH ₃
----	Pentane	CH ₃ (CH ₂) ₃ CH ₃
----	Isopentane	CH ₃ CH(CH ₃)CH ₂ CH ₃
----	Neopentane	CH ₃ C(CH ₃) ₂ CH ₃
----	Cyclopentane	-(CH ₂) ₅ -
<i>Fluorocarbons</i>		
13I1	Iodotrifluoromethane	CF ₃ I
----	Pentafluorodimethyl ether	CF ₂ OCF ₂ H
152a	1,1-difluoroethane	CH ₃ CHF ₂
161	Fluoroethane	CH ₃ CH ₂ F
218	Hexafluoroethane	CF ₃ CF ₃
<i>Oxygen compounds</i>		
----	Dimethyl ether	CH ₃ OCH ₃
610	Ethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃
----	Poly butylene glycols	H-(O-CH ₃ CH ₂ CH ₂ CH ₃) _n -OH
611	Methyl formate	HCOOCH ₃
<i>Inorganic Compounds</i>		
744	Carbon dioxide	CO ₂
764	Sulfur hexafluoride	SF ₆
<i>Unsaturated Organic Compounds</i>		
1150	Ethene (ethylene)	CH ₂ =CH ₂
1270	Propene (propylene)	CH ₃ CH=CH ₂

Table III: Refrigerant Mixtures

Refrigerant Number	Composition (Wt.%)
<i>Zeotropes</i>	
400	R-12/114 (40/60)
401A	R-22/152a/124 (53/13/34)
401B	R-22/152a/124 (61/11/28)
401C	R-22/152a/124 (33/15/52)
402A	R-125/290/22 (60/2/38)
402B	R-125/290/22 (38/2/60)
403A	R-290/22/218 (5/75/20)
403B	R-290/22/218 (5/56/39)
404A	R-125/143a/134a (44/52/4)
405A	R-22/152a/142b/C318 (45/7/5.5/42.5)
406A	R-22/600a/142b (55/4/41)
407A	R-32/125/134a (20/40/40)
407B	R-32/125/134a (10/70/20)
407C	R-32/125/134a (23/25/52)
407D	R-32/125/134a (15/15/70)
407E	R-32/125/134a (25/15/60)
408A	R-125/143a/22 (7/46/47)
409A	R-22/124/142b (60/25/15)
409B	R-22/124/142b (65/25/10)
410A	R-32/125 (50/50)
410B	R-32/125 (45/55)
411A	R-1270/22/152a) (1.5/87.5/11.0)
411B	R-1270/22/152a (3/94/3)
412A	R-22/218/143b (70/5/25)
413A	R-218/134a/600a (9/88/3)
414A	R-22/124/600a/142b (51/28.5/4/16.5)
414B	R-22/124/600a/142b (50/39/1.5/9.5)
<i>Azeotropes</i>	
500	R-12/152a (73.8/26.2)
501	R-22/12 (75.0/25.0)
502	R-22/115 (48.8/51.2)
503	R-23/13 (40.1/59.9)
504	R-32/115 (48.2/51.8)
505	R-12/31 (78.0/22.0)
506	R-31/114 (55.1/44.9)
507A	R-125/143a (50/50)
508A	R-23/116 (39/61)
508B	R-23/116 (46/54)
509A	R-22/218 (44/56)

Table IV: Hydrofluorocarbon Refrigerant Mixtures

Mixture #	R-32 wt.%	R-125 wt.%	R-143a wt.%	R-134a wt.%
1	10 to 80	90 to 20	-	-
2	5 to 45	5 to 45	-	90 to 10
3	-	30 to 90	70 to 10	-
4	-	60 to 40	39 to 20	2 to 40

5 The compositions of the present invention may comprise any specific combination of any one or more refrigerants listed in Table I, Table III, and/or Table IV with any one or more solubilizing agents listed in Table II. Therefore, each and every possible specific combination of listed refrigerants and solubilizing agents is considered independently enabled as an embodiment of the present invention.

10

The components of the composition of the invention are known materials that are commercially available or may be prepared by known methods. Preferably, the components are of sufficiently high purity so as to avoid the introduction of adverse influences on the properties of the system.

15

The compositions of the invention may also contain additives such as oxidation resistance and thermal stability enhancers, corrosion inhibitors, metal deactivators, lubricity additives, viscosity index enhancers, pour and/or floc point depressants, detergents, dispersants, antifoaming agents, anti-wear agents, and 20 extreme pressure resistant additives. Many additives are multifunctional. For example, certain additives may impart both anti-wear and extreme pressure resistance properties, or function both as a metal deactivator and a corrosion inhibitor. Cumulatively, all additives preferably do not exceed 8% by weight, or more 25 preferably do not exceed 5% by weight, of the total composition.

25

An effective amount of the foregoing additive types is generally in the range from 0.01 to 5% for the antioxidant component, 0.01 to 5% for the corrosion inhibitor component, from 0.001 to 0.5% for the metal deactivator component, from 0.5 to 5% for the lubricity additives, from 0.01 to 2% for each of the viscosity index enhancers 30 and pour and/or floc point depressants, from 0.1 to 5% for each of the detergents and dispersants, from 0.001 to 0.1% for anti-foam agents, and from 0.1-2% for each of the

anti-wear and extreme pressure resistance components. All these percentages are by weight and are based on the total composition. It is to be understood that more or less than the stated amounts of additives may be more suitable to particular circumstances, and that a single molecular type or a mixture of types may be used for each type of 5. additive component. Also, the examples listed below are intended to be merely illustrative and not limiting.

Examples of suitable oxidation resistance and thermal stability enhancers are diphenyl-, dinaphthyl-, and phenylnaphthyl-amines, in which the phenyl and naphthyl 10 groups can be substituted, e.g., N,N'-diphenyl phenylenediamine, p-octyldiphenylamine, p,p-dioctyldiphenylamine, N-phenyl-1-naphthyl amine, N-phenyl-2-naphthyl amine, N-(p-dodecyl)phenyl-2-naphthyl amine, di-1-naphthylamine, and di-2-naphthylamine; phenothiazines such as N-alkylphenothiazines; imino(bisbenzyl); and hindered phenols such as 6-(t-butyl) 15 phenol, 2,6-di-(t-butyl) phenol, 4-methyl-2,6-di-(t-butyl) phenol, 4,4'-methylenebis(2,6-di-{t-butyl} phenol), and the like.

Examples of suitable cuprous metal deactivators are imidazole, benzimidazole, 2-mercaptopbenzthiazole, 2,5-dimercaptothiadiazole, salicylidine- 20 propylenediamine, pyrazole, benzotriazole, tolutriazole, 2-methylbenzimidazole, 3,5-imethyl pyrazole, and methylene bis-benzotriazole. Benzotriazole derivatives are preferred. Other examples of more general metal deactivators and/or corrosion inhibitors include organic acids and their esters, metal salts, and anhydrides, e.g., N-oleyl-sarcosine, sorbitan mono-oleate, lead naphthenate, dodecetyl-succinic acid 25 and its partial esters and amides, and 4-nonylphenoxy acetic acid; primary, secondary, and tertiary aliphatic and cycloaliphatic amines and amine salts of organic and inorganic acids, e.g., oil-soluble alkylammonium carboxylates; heterocyclic nitrogen containing compounds, e.g., thiadiazoles, substituted imidazolines, and oxazolines; quinolines, quinones, and anthraquinones; propyl gallate; barium dinonyl naphthalene 30 sulfonate; ester and amide derivatives of alkenyl succinic anhydrides or acids, dithiocarbamates, dithiophosphates; amine salts of alkyl acid phosphates and their derivatives.

Examples of suitable lubricity additives include long chain derivatives of fatty acids and natural oils, such as esters, amines, amides, imidazolines, and borates.

Examples of suitable viscosity index enhancers include polymethacrylates, 5 copolymers of vinyl pyrrolidone and methacrylates, polybutenes, and styrene-acrylate copolymers.

Examples of suitable pour point and/or floc point depressants include polymethacrylates such as methacrylate-ethylene-vinyl acetate terpolymers; alkylated 10 naphthalene derivatives; and products of Friedel-Crafts catalyzed condensation of urea with naphthalene or phenols.

Examples of suitable detergents and/or dispersants include polybutenylsuccinic acid amides; polybutenyl phosphonic acid derivatives; long chain 15 alkyl substituted aromatic sulfonic acids and their salts; and metal salts of alkyl sulfides, of alkyl phenols, and of condensation products of alkyl phenols and aldehydes.

Examples of suitable anti-foam agents include silicone polymers and some 20 acrylates.

Examples of suitable anti-wear and extreme pressure resistance agents include sulfurized fatty acids and fatty acid esters, such as sulfurized octyl tallate; sulfurized terpenes; sulfurized olefins; organopolysulfides; organo phosphorus derivatives 25 including amine phosphates, alkyl acid phosphates, dialkyl phosphates, aminedithiophosphates, trialkyl and triaryl phosphorothionates, trialkyl and triaryl phosphines, and dialkylphosphites, e.g., amine salts of phosphoric acid monohexyl ester, amine salts of dinonylnaphthalene sulfonate, triphenyl phosphate, trinaphthyl phosphate, diphenyl cresyl and dicresyl phenyl phosphates, naphthyl diphenyl 30 phosphate, triphenylphosphorothionate; dithiocarbamates, such as an antimony dialkyl dithiocarbamate; chlorinated and/or fluorinated hydrocarbons, and xanthates.

ExamplesExample 1

Critical flammability ratio (CFR) of mixtures determined using Underwriter Laboratories Refrigerant Flammability test method 2182. CFR allows determination of what level of flammable material can be incorporated, without the mixture itself becoming flammable. Butane and dimethyl ether (DME) were added to R-407C (23 wt.% R-32; 25 wt.% R-125 and 52 wt.% R-134a) as the flammable additive.

Temp. (°C)	Additive	Wt.%
25	Butane	3.4
60	Butane	3.1
100	Butane	2.5
25	DME	3.3
60	DME	2.7
100	DME	2.1

10 The table indicates that certain 32/125/134a/butane (or DME) compositions are nonflammable per the widely used refrigerant flammability method.

Example 2

15 Actual testing in a refrigeration machine of a composition of the invention (test mixture: 22.5 wt.% R-32, 24.5 wt.% R-125, 51 wt.% R-134a, 2 wt.% butane) was performed under typical air conditioning conditions and using mineral oil supplied by the compressor manufacturer (Copeland blended white oil Catalog No. 999-5170-31).

20 Testing was performed in a 2 ton air conditioner system setup similar to the unit reported in Report DOE/CE/23810-71 "Study of Lubricant Circulation in HVAC Systems," March 1995-April 1996 (author Frank R. Biancardi et. al.; prepared for Air Conditioning and Refrigeration Technology Institute Under ARTI/MCLR Project No. 665-53100) except that instead of equal size risers, three different size risers (3/4", 7/8" and 1 1/8") were used to allow a greater variety of velocities. Also the ability to pump oil from the compressor sump into the compressor discharge line was added. Using a hand pump, 90cc of oil from the sump was injected into the

compressor discharge line. By observing the oil level in the compressor sump versus time, the rate and time required for oil return was measured.

Composition	Capacity (tons)	COP	Oil return rate (cc/min)	Completion Time (min)
R-407C	1.70	2.9	2.4	65
Test Mixture	1.88	3.3	2.7	46

5 Oil return is important for compressor reliability purposes. The example demonstrates that both capacity and efficiency of the system are enhanced over R-407C in the absence of the solubilizing agent and the oil return is improved as well (in mineral oil systems).

10 Examples 3-7

The performance of mixtures of HFC refrigerant R-407C is obtained in the presence and absence of solubilizing agents in a thermodynamic refrigeration cycle operating in typical air conditioning application (100°F condensing temperature and 15 40°F evaporating temperature). The vapor pressure of each mixture is measured at 25°C.

Ex. No.	32/125/134a Refrigerant Mixture (wt.%)	Solubilizing agent	Wt.%	Refrigeration Capacity relative to R-407C	Vapor Pressure relative to R-407C (25°C)	Oil Return
3	23/25/52 (R-407C)	--	0	1	1	No
4	21.9/23.8/49.3	Propane	5	1.05	1.05	Yes
5	21.9/23.8/49.3	Butane	5	1.00	0.99	Yes
6	22.6/24.5/51.0	Butane	2	1.00	1.00	Yes
7	20.9/22.7/47.4	Butane	10	1.00	0.98	Yes

Example 3 demonstrates that the HFC itself is unsuitable for use with hydrocarbon oil in that without oil return the compressor may be damaged.

Example 4 demonstrates that although there is oil return, the addition of propane results in an undesirable increase in the pressure of the system.

5 Examples 5-7 demonstrate that the use of butane results in oil return without an undesirable pressure increase. This is particularly important for retrofitting applications.

What is claimed is:

1. A composition comprising:
 - (i) a refrigerant selected from the group consisting of trichlorofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, tetrafluoromethane, dichlorofluoromethane, chlorodifluoromethane, trifluoromethane, dichloromethane, chlorofluoromethane, difluoromethane, chloromethane, fluoromethane, 1,1,2-trichloro-1,2,2-trifluoromethane, 1,2-dichloro-1,1,2,2-tetrafluoromethane, chloropentafluoroethane, hexafluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1-dichloro-1-fluoroethane, 1,1-chloro-1,1-difluoroethane, 1,1,1-trifluoroethane, octafluoropropane, 1,1,1,2,3,3,3-heptafluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, and octafluorocyclobutane, and mixtures of two or more thereof; and (ii) a solubilizing agent selected from the group consisting of dichloromethane, chloromethane, methane, ethane, propane, butane, isobutane, pentane, isopentane, neopentane, cyclopentane, iodotrifluoromethane, pentafluorodimethyl ether, 1,1-difluoroethane, fluoroethane, hexafluoroethane, dimethyl ether, ethyl ether, polybutylene glycols, methyl formate, carbon dioxide, sulfur hexafluoride, ethylene, propylene, and mixtures of two or more thereof.
2. The composition of claim 1 wherein the refrigerant comprises a compound selected from the group consisting of R-32, R-125, R-134a, R-143a and mixtures of two or more thereof.
3. The composition of claim 1 wherein the refrigerant is a mixture of R-32, R-125 and R-134a.
4. The composition of claim 1 wherein the refrigerant is a mixture of R-32 and R-125.

5. The composition of claim 1 wherein the refrigerant is a mixture of R-143a, R-125 and R-134a.
6. The composition of claim 1 wherein the refrigerant is a mixture of R-125 and R-143a.
- 5 7. The composition of claim 1 wherein the refrigerant is selected from the group consisting of R-400, R-401A, R-401B, R-401C, R-402A, R-402B, R-403A, R-403B, R-404A, R-405A, R-406A, R-407A, R-407B, R-407C, R-407D, R-407E, R-408A, R-409A, R-409B, R-410A, R-410B, R-411A, R-411B, R-412A, R-413A, R-414A, R-414B, R-500, R-501, 4-502, R-503, 10 4-504, R-505, R-506, R-507A, R508A, R-508B, R-509A, and mixtures of two or more thereof.
8. The composition of claim 1 wherein the refrigerant is selected from the group consisting of R-404A, R-407C, R-410A and R-507A.
9. The composition of claim 1 wherein the refrigerant is selected from the 15 group consisting of:
 - (a) a mixture of from 10 to 80 wt.% R-32 and from 90 to 20 wt.% R-125;
 - (b) a mixture of from 5 to 45 wt.% R-32, from 5 to 45 wt.% R-125 and from 90 to 10 wt.% R-134a;
 - (c) a mixture of from 30 to 90 wt.% R-125 and from 70 to 10 wt.% R-20 143a; and
 - (d) a mixture of from 60 to 40 wt.% R-125, from 39 to 20 wt.% R-143a, and from 2 to 40 wt.% R-134a.
10. The composition of any one of claims 1-9 wherein the solubilizing agent is butane.
- 25 11. The composition of any one of claims 1-9 wherein the solubilizing agent is isobutane.

12. The composition of any one of claims 1-9 wherein the solubilizing agent is pentane.
13. The composition of any one of claims 1-9 wherein the solubilizing agent is dimethyl ether.
- 5 14. The composition of claim 1 further comprising a lubricating oil selected from the group consisting of mineral or hydrocarbon oil, alkyl benzene oil, white or paraffinic oil and mixtures thereof.
- 10 15. A method for producing refrigeration which comprises condensing the composition of claim 1 and thereafter evaporating the composition in the vicinity of a body to be cooled.
16. A method for producing heating which comprises condensing the composition of claim 1 in the vicinity of a body to be heated and thereafter evaporating the composition.
17. A process for heating or cooling comprising the step of using the mixture of claim 1 as a heat transfer media.
- 15 18. A sterilizing gas composition comprising effective amounts of the composition of claim 1 and ethylene oxide.
19. A method of sterilizing articles comprising exposing the articles to the sterilizing gas composition of claim 18.
- 20 20. A method of dissolving contaminants or removing contaminants from the surface of a substrate which comprises the step of using a composition comprising the composition of claim 1 as a solvent.
21. A process for suppressing a fire comprising a step of using the mixture of claim 1 as a fire extinguishing agent.
- 25 22. A blowing agent composition comprising the composition of claim 1.

23. A method for producing polyurethane and polyisocyanurate foams comprising reacting and foaming a mixture of ingredients that react to form the polyurethane and polyisocyanurate foams in the presence of a volatile blowing agent comprising the composition of claim 1.
5. 24. A premix of a polyol and a blowing agent comprising the composition of claim 1.
25. A closed cell foam composition prepared by foaming a polyisocyanate or polyisocyanurate in the presence of a blowing agent comprising the composition of claim 1.
- 10 26. A process for atomizing a fluid comprising using the composition of claim 1 as an aerosol propellant.
27. A process for electrically insulating comprising using the composition of claim 1 as a gaseous dielectric.
28. A method of recharging a refrigeration system of the type containing a chlorine-containing refrigerant and a lubricating oil, comprising the steps of:
 - (a) removing said chlorine-containing refrigerant from said refrigeration system while leaving substantially all of said lubricating oil in said system; and
 - 20 (b) introducing to said lubricating oil left in said system the composition of claim 1.

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A3

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(54) Title: FLUOROCARBON REFRIGERANT COMPOSITIONS

(57) Abstract: The invention provides fluorocarbon refrigerant compositions that offer alternatives, and are considered environmentally safe substitutes, for CFC's and HCFC's. The compositions of the invention are useful as refrigerants, including for use in chillers, aerosol propellants, metered dose inhalers, heat transfer media, gaseous dielectrics, fire extinguishing agents, foam blowing agents, solvents and sterilants. The compositions of the invention are soluble in lubricating oils and are, therefore, particularly useful as R-22 retrofit fluids.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K5/04 C09K3/30 C08J9/14 C23G5/028

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 659 862 A (SANYO ELECTRIC CO) 28 June 1995 (1995-06-28) the whole document ---	1-3,9, 12,14-17
X	EP 0 779 352 A (AUSIMONT SPA) 18 June 1997 (1997-06-18) the whole document ---	1,2,10, 11, 14-17,28
X	WO 96 03473 A (MURPHY FREDERICK THOMAS ;CORR STUART (GB); ICI PLC (GB); MORRISON) 8 February 1996 (1996-02-08) the whole document ---	1-6,9, 12,14-17
X	US 5 688 432 A (PEARSON STEPHEN FORBES) 18 November 1997 (1997-11-18) the whole document ---	1,2,11, 14-17,28 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 670 079 A (LUNGER BROOKS SHAWN ET AL) 23 September 1997 (1997-09-23) the whole document ---	1,2, 14-17, 20,22
X	DE 42 26 431 A (PRIVATE INST FUER LUFT UND KA) 17 February 1994 (1994-02-17) the whole document ---	1,2, 13-17
X	EP 0 638 623 A (AUSIMONT SPA) 15 February 1995 (1995-02-15) the whole document ---	1,2, 13-17
X	DATABASE WPI Section Ch, Week 199742 Derwent Publications Ltd., London, GB; Class E19, AN 1997-454151 XP002194080 & JP 09 208940 A (SANYO ELECTRIC CO LTD), 12 August 1997 (1997-08-12) abstract ---	1,2,9,12
X	WO 97 15637 A (HAN LIZHONG ;UNIV TSINGHUA (CN); ZHAO XIAOYU (CN); YE MAO (CN); ZH) 1 May 1997 (1997-05-01) abstract ---	1,2, 14-17
P,X	WO 00 56834 A (DU PONT) 28 September 2000 (2000-09-28) the whole document ---	1-3, 7-12, 14-17, 20,22

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-28 relate to an extremely large number of possible compositions of a refrigerant (i) and a solubilizing agent (ii) and processes using said compositions. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compositions and processes claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compositions prepared in the examples 1,2,4-7 wherein the refrigerant (i) is a mixture of R-32, R-125 and R-134a and a reasonable generalisation thereof.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No	
PCT/US 01/30276	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0659862	A 28-06-1995	JP 7173460 A		11-07-1995
		CN 1317533 A		17-10-2001
		CN 1108290 A		13-09-1995
		DE 69410966 D1		16-07-1998
		DE 69410966 T2		08-10-1998
		EP 0659862 A1		28-06-1995
		US 2001017364 A1		30-08-2001
EP 0779352	A 18-06-1997	IT MI952627 A1		16-06-1997
		EP 0779352 A1		18-06-1997
WO 9603473	A 08-02-1996	AT 205872 T		15-10-2001
		AU 698733 B2		05-11-1998
		AU 2988795 A		22-02-1996
		BR 9508347 A		30-09-1997
		CA 2195411 A1		08-02-1996
		DE 69522811 D1		25-10-2001
		DK 772659 T3		26-11-2001
		EP 0772659 A1		14-05-1997
		ES 2163520 T3		01-02-2002
		WO 9603473 A1		08-02-1996
		JP 10503230 T		24-03-1998
US 5688432	A 18-11-1997	AU 7660994 A		10-04-1995
		DE 69403809 D1		17-07-1997
		DE 69403809 T2		22-01-1998
		EP 0720639 A1		10-07-1996
		JP 9503800 T		15-04-1997
US 5670079	A 23-09-1997	US 5458798 A		17-10-1995
		AU 6096594 A		29-08-1994
		CN 1174970 A		04-03-1998
		EP 1028152 A2		16-08-2000
		EP 0682683 A1		22-11-1995
		JP 8506581 T		16-07-1996
		WO 9418282 A1		18-08-1994
		US 5624596 A		29-04-1997
		US 5635098 A		03-06-1997
		CN 1119454 A		27-03-1996
DE 4226431	A 17-02-1994	DE 4226431 A1		17-02-1994
EP 0638623	A 15-02-1995	IT MI931829 A1		13-02-1995
		AT 174374 T		15-12-1998
		DE 69415099 D1		21-01-1999
		DE 69415099 T2		29-04-1999
		EP 0638623 A1		15-02-1995
JP 9208940	A 12-08-1997	NONE		
WO 9715637	A 01-05-1997	CN 1148613 A		30-04-1997
		CN 1162616 A		22-10-1997
		AU 7276996 A		15-05-1997
		WO 9715637 A1		01-05-1997
WO 0056834	A 28-09-2000	EP 1163313 A1		19-12-2001
		WO 0056834 A1		28-09-2000